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Research Paper

Assessing human metal accumulations in an urban superfund site

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ABSTRACT

Butte, Montana is part of the largest superfund site in the continental United States. Open-pit mining continues in close proximity to Butte's urban population. This study seeks to establish baseline metal concentrations in the hair and blood of individuals living in Butte, MT and possible routes of exposure. Volunteers from Butte ($n = 116$) and Bozeman ($n = 86$) were recruited to submit hair and blood samples and asked to complete a lifestyle survey. Elemental analysis of hair and blood samples was performed by ICP-MS. Three air monitors were stationed in Butte to collect particulate and filters were analyzed by ICP-MS. Soil samples from the yards of Butte volunteers were quantified by ICP-MS. Hair analysis revealed concentrations of Al, As, Cd, Cu, Mn, Mo, and U to be statistically elevated in Butte's population. Blood analysis revealed that the concentration of As was also statistically elevated in the Butte population. Multiple regression analysis was performed for the elements As, Cu, and Mn for hair and blood samples. Soil samples revealed detectable levels of As, Pb, Cu, Mn, and Cd, with As and Cu levels being higher than expected in some of the samples. Air sampling revealed consistently elevated As and Mn levels in the larger particulate sampled as compared to average U.S. ambient air data.

1. Introduction

Butte, MT a town with over a century of copper and molybdenum mining activities is home to approximately 30,000 individuals and is also part of the largest Superfund complex in the United States to date. Butte was given Superfund designation in 1983. In 1994 the United States Environmental Protection Agency (EPA) issued a Record of Decision designating Butte, along with the neighboring town and mining site of Anaconda, MT, and 120 miles of Montana's Clark Fork River, as a single Superfund complex (EPA, 1994). The EPA identified potential health threats from direct contact with, or ingestion of, contaminated soils, water, or inhalation of contaminated air (EPA, 1994). Epidemiological studies conducted in the 1990s and the early 2000s suggested that cancer rates (National Cancer Institute, 2009), as well as neurodegenerative diseases (e.g. Multiple sclerosis, Parkinson's disease) (Satterly, 1995), are higher than average in Butte (Silver-Bow County) as compared to the rest of Montana and the nation. More current epidemiological reports from The National Cancer Institute now list Silver Bow County as a priority 8, or declining trend, county (National Cancer Institute, 2017). In addition to the historical mining activity and waste, current open-pit mining activities continue to occur within the city limits of Butte. While most studies have focused on the historical waste issues in Butte, little is known about the effects of current surface copper and molybdenum mining within the city limits.

Exposure assessment is often considered the weakest link in risk assessment (Kakkar and Jaffery, 2005). However, the relationship between exposure of a population to a pollutant and the subsequent biological effect is an important aspect of environmental epidemiology. Metals are known to cause a variety of disease states depending on the amount and type of metal exposure, the length of exposure time, and the individuals' genetic predisposition (Yoon et al., 2008; Jomova and Valko, 2011). Chronically high levels of redox active metals are known to participate in inflammatory response and oxidative stress (Gaetke and Chow, 2003). In addition, aberrant levels of metals, such as high copper and low zinc, are implicated in a variety of diseases, especially neurodegenerative diseases (Lim et al., 2010). Many metals or metalloids, such as lead, mercury, cadmium and arsenic can lead to toxic effects in humans, even at low levels of exposure (Zhang et al., 2015). Metals that are essential trace micronutrients, such as copper, zinc and manganese, have been implicated in protein dysregulation and disease

Abbreviations: ICP-MS, inductively coupled plasma–mass spectrometry; TSP, total suspended particulate; ppm, parts per million; ppb, parts per billion; Al, aluminum; As, arsenic; Cd, cadmium; Cu, copper; Pb, lead; Mn, manganese; Mo, molybdenum; U, uranium; Zn, zinc

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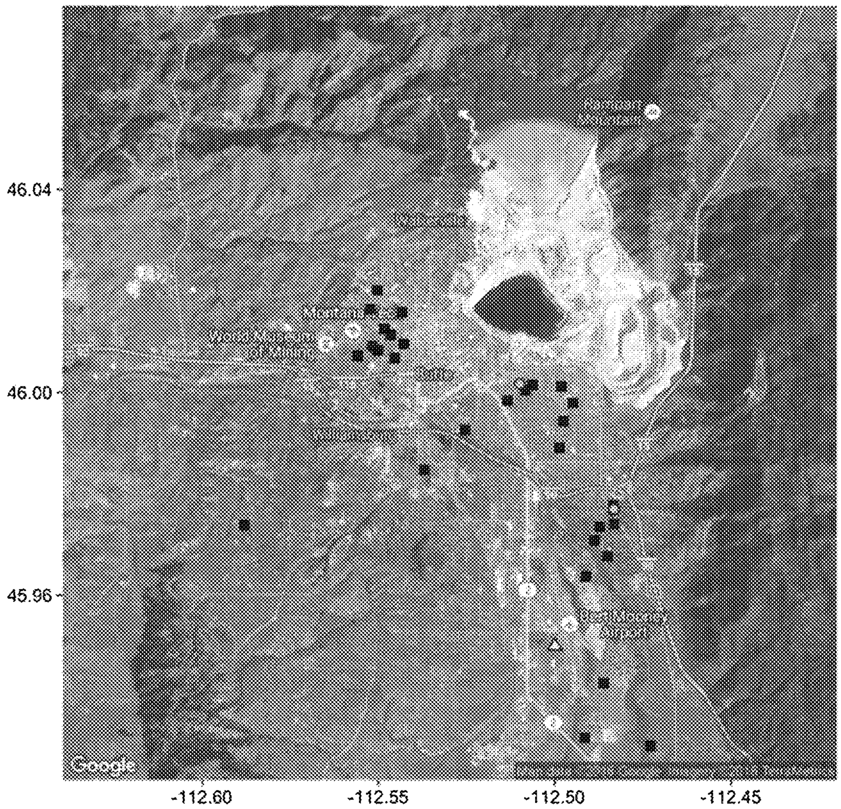

Fig. 1. Butte, MT study area wherein soil (blue squares) and air (green circles) samples were collected. Soil samples were collected once and air samples were collected weekly during the period of May–October 2015. Weather information collected at Bert Mooney Airport weather station (yellow triangle). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

states when found in elevated concentrations outside of the optimum range (Gaetke and Chow, 2003).

Very little human sampling has been undertaken in Butte, MT, the nation's largest Superfund Site, and an area with extensive and ongoing metal contaminate release to the environment. This study seeks to establish current metal concentrations in individuals living within close proximity to the surface copper mine in Butte, MT by sampling both blood and hair of volunteers. To date, no study has evaluated the contribution to metal exposures through inhalation or ingestion of dust from the surface mine in the presence of other primary pathways, such as smoking or diet. Additionally, correlations among different metals, which may reveal potential antagonistic or synergetic sources, have been completely unexplored.

Butte, MT sits at an elevation of approximately 5500 ft above sea level, has a semi-arid climate, and is surrounded on three sides by the Continental Divide. Open pit mining began in 1955 with the creation of the Berkeley Pit which operated until 1982. Superfund designation was given in 1983 and then interestingly the Continental Pit, which is adjacent and to the east of the Berkeley Pit, opened in 1986 (Pit Watch, 2016). The Continental Pit is still currently in operation. Fig. 1 is a Google Earth image illustrating the layout of the town of Butte as well as the size and location of the Berkeley Pit, Continental Pit, and the Tailings Pond north of town. In addition, locations 1 and 2 (Fig. 1, green circles) are identified on the map as the 2 locations of the air monitoring stations that were in use from May 2015–October 2015. Other locations mapped show approximate locations of soil samples that were collected throughout town (Fig. 1, blue squares).

This study seeks to establish baseline metal accumulations in the Butte population through a variety of mechanisms. First, volunteers were recruited from Butte to submit hair and blood samples to be digested and analyzed for metal content by inductively-coupled plasma mass spectrometry (ICP-MS). These data were compared to a control population of volunteers recruited from Bozeman, MT (Gallatin County). Bozeman is a town approximately 90 miles to the east of Butte with no historical or current mining practices.

Biological monitoring is a commonly used method to assess the potential accumulation of emissions in a population. Blood, urine, feces, hair and nails are all biological materials that are commonly used to quantify trace metal accumulations (Elinder et al., 1988; Kucera et al., 1995) and all methods have advantages and limitations in their use. One of the major limitations in biological monitoring is the lack of correlation of a trace element between matrices type (i.e. hair vs blood or whole blood vs serum) (Hall et al., 2006; Schultze et al., 2014) with blood giving information for acute exposure (Pomroy et al., 1980) and hair as a way to monitor longer exposure times (Bencko, 1995; Iyengar, 1998; Klaassen, 2001). Hair is an attractive, non-invasive, highly mineralized biological monitoring source that reflects minerals and chemicals contained in the organism. This means that hair elemental concentrations correlate well to the actual internal levels of those chemical substances in the body (Szynkowska et al., 2015).

In addition to the human sampling, soil samples were collected from residences of 32 of the Butte volunteers. Soil samples were dried, sieved, acid digested and analyzed for metal content by ICP-MS. To more fully understand the potential environmental routes of exposure, three air monitors were placed in two locations in Butte from late May–October 1, 2015. These three monitors were set to continuously collect either PM 10 μm or total suspended particulate (TSP). Large air particles, PM 10 and larger, were monitored in this study since dust production from the current mining activity is of major concern rather than combustion of particles into the smaller, 2.5 μm particle size. Each week, the air filters were weighed and portions were acid digested and analyzed for metal content by ICP-MS.

Data collected suggests that current open-pit mining practices within the city limits of Butte, MT may be causing chronic inhalation and/or ingestion of low levels of various metals. Both hair and blood data revealed elevated levels of As in the Butte population as compared to Bozeman. In addition, Al, Cu, Cd, Mn, Mo, and U were found to be elevated in hair samples of Butte residents as compared to Bozeman residents. These elevated metals could be associated with aberrant biological regulation of important enzymatic and biological cofactors which, in turn, may impact human health.

2. Materials and methods

2.1. Volunteer recruitment

Butte volunteers were screened based on the following criteria: at least 18 years of age, and have lived in Butte, MT for a minimum of 6 consecutive months. Bozeman volunteers were chosen based on similar criteria, barring persons having lived in Butte for any period of time. A total of 202 volunteers were selected for the study, 116 from Butte and 86 from Bozeman. Each volunteer signed a consent form prior to participating and filled out a lifestyle survey which covered basic health questions including BMI and smoking status. Additionally, participants were asked about their diet, exercise, and disease status. The majority of the volunteers were recruited at blood drives run by United Blood Services.

2.2. Hair sampling

Each volunteer was asked to submit a scalp hair sample for metal analysis. A minimum of 0.15 g of hair was collected from each volunteer. Hair was collected from as close to the scalp as possible with each sample containing hair from 2 to 3 locations of the posterior vertex. Samples were stored in paper envelopes until analysis. The hair samples were sent to an off-site laboratory, Trace Elements Inc., acid digested and analyzed by ICP-MS for a suite of 36 elements. All 116 samples from Butte and 86 samples from Bozeman were collected and analyzed for metal content.

2.3. Blood sampling

One hundred fifty-three of the volunteers, 81 from Butte and 72 from Bozeman, had 1–2 mL of blood collected by venous puncture into a glass tube filled with 7.5% K_2-EDTA and stored at room temperature until digestion. Following Tekran application note: AN2600-10, one milliliter of blood was placed in a Teflon digester tube. Three milliliters of concentrated nitric acid (trace metal grade, BDH VWR Analytical) and 1.5 mL of ultra-pure water were placed in the tube with the blood and samples were heated at 85 °C for 4 h. At the end of the first heating, samples were removed from the heat block, cooled to room temperature, and 1.0 mL of 30% H_2O_2 (trace metal grade, KMG) was added to each sample. Samples were then returned to the heat block at 70 °C for 30 min. At the end of the second incubation, samples were removed from the heat blocks and cooled to room temperature. Samples were diluted to 50 mL with ultra-pure H_2O and analyzed by ICP-MS for eleven elements. Analysis was performed utilizing a Perkin-Elmer ELAN DRC II ICP-MS (Bradford, CT USA) for measurement. The analysis followed EPA method 200.8 protocol (Creed et al., 1994), modified for the use of a dynamic reaction cell (DRC) to eliminate polyatomic interferences on arsenic and manganese.

2.4. Soil sampling

To investigate potential environmental sources of metals, soil and air samples were collected from Butte. From 32 of the Butte volunteers, soil samples were collected following a procedure outlined by the Montana Department of Environmental Quality (MT-DEQ) (MTDEQ, 2013). Briefly, approximately one-inch of undisturbed top soil was collected by hand trowel and placed in a plastic bag. Soil was returned to the lab and opened to the atmosphere in order to dry. Once dry, approximately 0.1 g of dried soil was sieved to 250 μm size. The soil was then weighed out, placed in a Teflon microwave digestion tube, and 9.8 mL HNO_3 and 0.2 mL HBF_4 were added to each sample. Soil was then digested using a MARS Express tissue digester following published protocols (Goddard and Brown, 2014). Briefly, samples were heated to 170 °C and held at that temperature for 15 min, using a maximum of 1400 W. Samples were then ramped to 225 °C, held for 30 min, again using a maximum of 1400 W. Samples were cooled to room temperature and then diluted to 50 mL with ultra-pure water, filtered, and analyzed by ICP-MS for 35 elements.

2.5. Air monitoring and sampling

Air sampling was undertaken within the Butte valley for four months starting in late May 2015 and continuing until October 1, 2015. Three air monitors were placed in two locations within the Butte valley (See Fig. 1). The first location, which was located approximately 0.5 miles south of the mine concentrator, contained two air monitors. One air monitor was set to select for 10 μm particulate and smaller, while the other collected total suspended particulate (TSP). Both monitors were set to run continuously, pulling 3 L/min of air through the device. The second location, which was approximately 2.5 miles south east of the mine concentrator, contained one monitor set to collect TSP and run continuously pulling 3 L/min of air.

Particulate was collected on a quartz filter which had been hydrated to a constant weight using a saturated calcium chloride solution. Once filters reached a constant weight, they were placed in the housing of the air monitor. Filters were changed weekly and rehydrated until reaching constant weight after collection. After reaching constant weight, approximately a third of the filter was cut out using ceramic scissors. Filters were digested using the sample protocol as described for the soil samples. After digestion, samples were diluted, filtered, and analyzed by ICP-MS for 11 elements utilizing a Perkin-Elmer ELAN DRC II ICP-MS (Bradford, CT USA) for measurement. The analysis followed EPA method 200.8 protocol (Creed et al., 1994), modified for the use of a dynamic reaction cell (DRC) to eliminate polyatomic interferences on arsenic and manganese.

2.6. Statistical analysis

All statistical analyses were performed using the R computing environment v.3.3.1 (R Core Team, 2016). Associations between Mn, Cu, and As concentration and covariates for age, gender, smoking status and site were investigated through the use of multiple regression. Because metal concentrations exhibited positive skew, all concentrations were $\log_{10}$ transformed. Preliminary log-level regression diagnostic plots indicated the presence of long-tailed error distributions. Since there existed no compelling reason to omit any observations on the basis of being extreme, robust regression was utilized to estimate parameter values. All log-level OLS regressions were refit using an *M*-estimator with the Huber weight function using the MASS package (Venables et al., 2002). Bias Corrected and adjusted (BCa) bootstrapped confidence intervals were computed using the car package (Fox and Weisber, 2011). Blood As concentration data were subject to left censoring due to limit of detection (i.e., < 5 ppb). To accommodate the left censoring, a tobit regression model was fit to the blood As data using the VGAM package (Yee, 2016).

3. Results

3.1. Volunteer demographics

Volunteers were recruited from Butte and Bozeman to participate in this study. Most volunteers were recruited from blood drives hosted by United Blood Services. Volunteers were asked to fill out lifestyle surveys as well as submitting hair and blood samples. Surveys collected age, gender, BMI, and smoking status as well as information regarding nutrition and exercise habits and personal and family disease history. As shown in Fig. 2, the Butte population of volunteers were older (median age = 50.5) and had a higher BMI (median = 25.84) than the Bozeman population (median age = 30.5, median BMI = 23.63). More females

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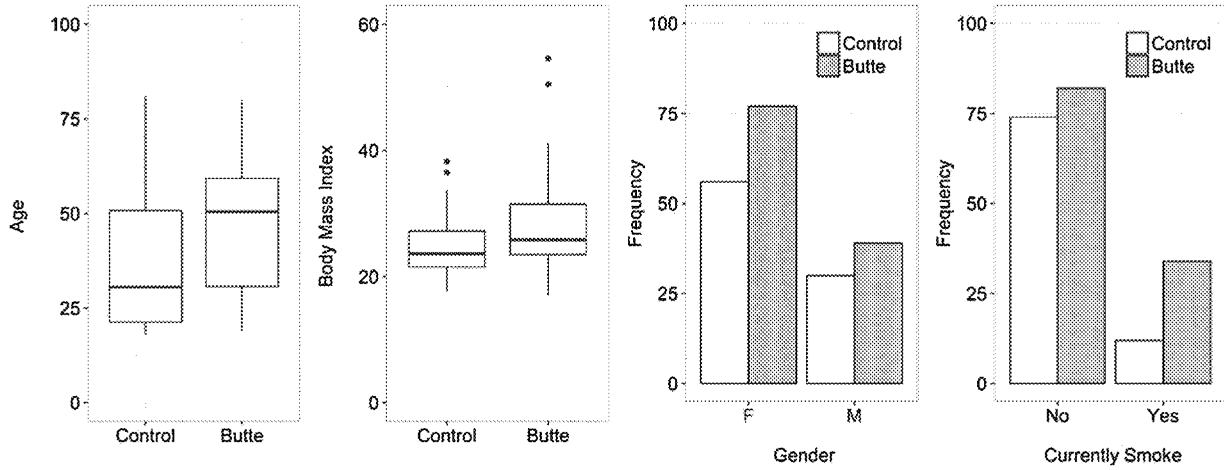

Fig. 2. Volunteer Demographics. Age, gender, body mass index, and smoking status information was collected from each volunteer and results are displayed as comparisons between locations (Butte vs. Bozeman). Body mass index measurements were not obtained for 10 individuals (Butte = 6, Bozeman = 4).

participated in the study than males from both locations (Butte: 39 men, 77 women; Bozeman: 30 men, 56 women). Butte had more smokers participate in the study than Bozeman but the gender distribution between the smoker subset was comparable between the two populations.

3.2. Hair results

202 hair samples, 116 from Butte and 86 from Bozeman, were analyzed for a suite of 36 elements by ICP-MS at an off-site facility, Trace Elements, Inc. Elements were quantified in mg/kg (ppm). As shown in Table 1, 11 elements of interest are shown with median and mean values and compared between groups. A nonparametric Wilcoxon rank-sum test was performed on all data. The elements Al, As, Cd, Cu, Mn, Mo, and U, were all found to be statistically different (α = 0.05) between Butte and Bozeman, with elevated concentrations in Butte's population.

3.3. Blood results

Blood samples were analyzed for 11 elements by ICP-MS. Of the 202 volunteers, 153 of the volunteers had sufficient quantity of blood taken for analysis. These data are represented in a similar fashion as the hair samples, in which elements are quantified and compared between groups. Statistical analysis was again performed using a nonparametric Wilcoxon Rank-Sum test. Arsenic was the only element found to be statistically different (α = 0.05) between Butte and Bozeman, with an elevated concentration in Butte's population. Table 2 illustrates the average μg/kg (ppb) concentration for each element analyzed, and when available, values are compared to published averages for that given element.

In Fig. 3, box and whisker plots were generated for Mn, Cu, and As concentrations found in hair. Fig. 3 also includes box and whisker plots for the concentrations of Mn and Cu found in blood samples. These box graphs represent the interquartile range (IQR), the middle 50% of the sample values, with the bolded horizontal line being the median. The "whiskers" extending out from the box represent the tails of the distribution and individual points represent extreme observations.

Table 1
ICP-MS analysis of 202 hair samples, 116 from Butte and 86 from Bozeman. Results for 11 elements of interest are represented as median and mean ppm between groups. "*" indicates distribution of element concentration in Butte is statistically different from that in Bozeman (α = 0.05) by Wilcoxon rank-sum test.

Element	Butte		Control	
	Median	Mean	Median	Mean
Aluminum*	5	7	3	5
Arsenic*	0.07	0.1	0.05	0.06
Cadmium*	0.03	0.06	0.02	0.04
Copper*	22	34	18	23
Lead	1	1.4	1	1.2
Manganese*	0.53	1	0.17	0.3
Molybdenum*	0.05	0.09	0.04	0.04
Selenium	41990	41533	43630	43371
Strontium	2.1	3.3	2.4	2.8
Uranium*	0.07	0.21	0.04	0.06
Zinc	170	196	180	211

Table 2
ICP-MS analysis of 153 blood samples, 81 from Butte and 72 from Bozeman. Results are represented in median ppb between groups. *As was found to be significant by Wilcoxon Rank-Sum analysis. NA = Published average for whole blood value unavailable. ([A] = The Mayo Clinic, 2017; [B] = CDC, 2017; [C] = Zhang et al., 2015; [D] = Burguera and Burguera, 2007).

Element	Butte	Control	Published Values
Aluminum	217.8	190.6	NA
Arsenic*	14.2	9.2	0–12[A]
Cadmium	nd	nd	0.33[B]
Copper	814.9	800.8	802.4[C]
Lead (μg/dL)	1.2	1	1.3[B]
Manganese	12.5	14.8	9.4[B]
Molybdenum	6.2	5.8	1.2–4.8[D]
Selenium	197.8	211.9	192[B]
Strontium	38.5	37.6	NA
Uranium	5.7	6.2	NA
Zinc	4911	5330	4665[C]

3.4. Regression analysis of As, Cu, and Mn

After controlling for age, gender, and smoking status, the estimated median hair metal concentration for Butte participants is elevated in comparison to Bozeman participants for Mn (95% CI: 1.77–3.36 times higher), Cu (95% CI: 1.02–1.40 times higher), and As (95% CI: 1.11–1.69 times higher). Controlling for the same covariates, we estimate the median blood Cu concentration to be depressed in Butte participants (95% CI: 0.88–0.98 times Bozeman participants) and find no statistical difference in median blood Mn concentration (Table 3). Using tobit regression, the estimated average blood As concentration for Butte participants was found to be elevated in comparison to Bozeman participants (95% CI: 1.20–5.18 ppb higher) (Table 4). Controlling for age, smoking status, and place of residence, the estimated median Cu concentration is depressed in male participants compared to

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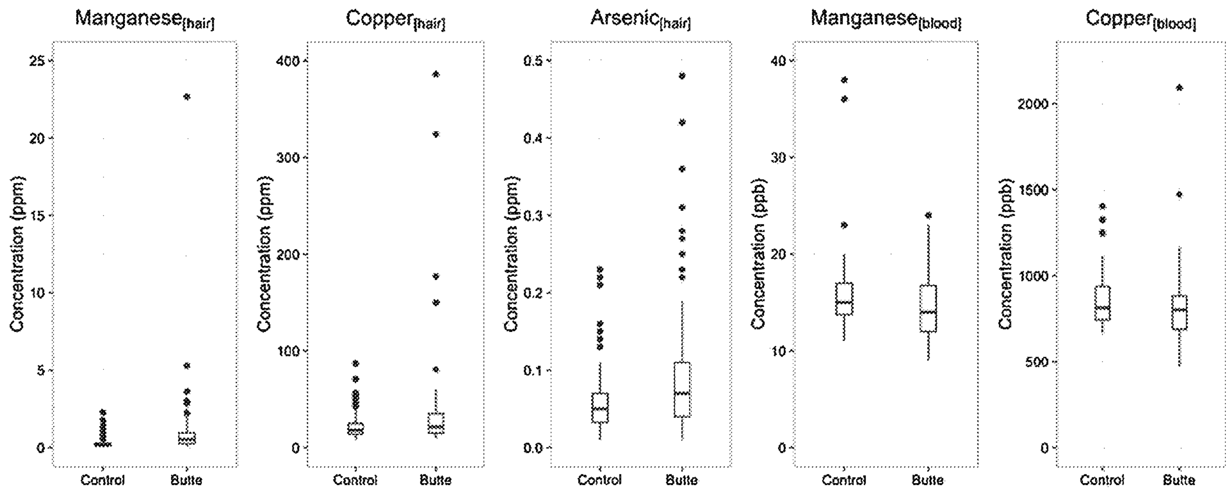

Fig. 3. Box and whisker plots for Mn, Cu, and As concentrations found in hair samples (n = 116 Butte, n = 86 Control) as well as Mn, and Cu values from blood samples (n = 81 Butte, n = 72 Control) between the two volunteer populations.

Table 3
Back-transformed estimates of regression coefficients in the robust multiple regression of $\log_{10}$ transformed metal concentration on age, gender, smoking status, and site covariates (intercept not displayed). BCa confidence intervals (back-transformed) based upon 10,000 bootstrap resamples.

Element	Covariate	Estimate	95% CI
Mn [hair]	age	1.0048	(0.9957, 1.0139)
$n_{Butte} = 116$	genderM	0.8863	(0.6751, 1.1719)
$n_{control} = 86$	smokeYes	1.3190	(0.9715, 1.8295)
	siteButte	2.4471	(1.7705, 3.3570)
Cu [hair]	age	1.0010	(0.9963, 1.0059)
$n_{Butte} = 116$	genderM	0.8005	(0.6843, 0.9297)
$n_{control} = 86$	smokeYes	0.9831	(0.8221, 1.2120)
	siteButte	1.1944	(1.0218, 1.4020)
As [hair]	age	1.0044	(0.9985, 1.0099)
$n_{Butte} = 116$	genderM	1.8785	(1.5153, 2.3188)
$n_{control} = 86$	smokeYes	1.1329	(0.9028, 1.4028)
	siteButte	1.3605	(1.1084, 1.6890)
Mn [blood]	age	0.9975	(0.9926, 0.9982)
$n_{Butte} = 50$	genderM	0.9446	(0.8468, 1.0288)
$n_{control} = 52$	smokeYes	0.9680	(0.8157, 1.0793)
	siteButte	0.9302	(0.8849, 1.0965)
Cu [blood]	age	1.0010	(0.9995, 1.0032)
$n_{Butte} = 80$	genderM	0.8394	(0.7964, 0.8845)
$n_{control} = 52$	smokeYes	1.0229	(0.9455, 1.1020)
	siteButte	0.9348	(0.8790, 0.9864)

Table 4
Estimates of regression coefficients in the tobit regression of blood As concentration on age, gender, smoking status, and site covariates (intercept not displayed) with respective Wald-type confidence intervals.

Element	Covariate	Estimate	95% CI
As [blood]	age	0.0656	(0.0073, 0.1338)
$n_{Butte} = 61$	genderM	1.1689	(−0.9705, 3.3083)
$n_{control} = 46$	smokeYes	0.6798	(−1.9545, 3.3142)
	siteButte	3.1937	(1.2042, 5.1831)

females for both hair (95% CI: 0.68–0.93 times females) and blood samples (95% CI: 0.80–0.88 times females). Furthermore, estimated median hair As concentration was found to be elevated in male participants (95% CI: 1.51–2.32 times females). No statistical difference in median metal concentration was found between participants differing in either age or smoking status, after controlling for all other covariates in the model.

3.5. Soil samples

Environmental samples were collected to determine a potential source of metal exposure for individuals living in Butte, MT. Soil samples were collected from the residences of 32 of the Butte volunteers. After digestion, samples were analyzed by ICP-MS for 35 elements. Of the 35 elements analyzed, 18 elements were compared to available MT DEQ background concentrations (Montana DEQ, 2013) for both Silver Bow and Gallatin counties (Table 5). In short, background concentrations were determined by MT DEQ by sampling 2 undisturbed locations in each county in the state of Montana.

3.6. Air monitoring

Air particulate collected over 18 weeks on the 3 air monitors was analyzed by ICP-MS and results were compared to available U.S. ambient air concentrations (32 EPA, 33 ATSDR). Fig. 4 shows representative graphs for two of the elements analyzed, As and Mn. For the 18-week period sampled, concentrations of these two elements were elevated over published typical US ambient air concentrations. It should be noted that Butte experienced a significant amount of wildfire smoke in the valley during collection weeks 12–14. It is possible that particulate in the smoke potentially positively skewed the metal content for those weeks.

4. Discussion

Butte, MT was once called "The Richest Hill on Earth", and produced enough copper to pave a four-lane highway four inches thick from Butte to Salt Lake City and 30 miles beyond [12]. The unique geology of Butte explains its past and current entanglement with underground and surface mining and the environmental ramifications that come from mining. This study sought to quantify metal accumulations in the hair and blood from individuals living in Butte, which is in close proximity to an active copper and molybdenum open pit mine as well as being part of the largest Superfund complex in the United States. Volunteers from Bozeman, MT, a city without historical or current mining, were recruited to submit control samples. 116 volunteers from Butte, MT and 86 volunteers from Bozeman, MT submitted hair samples for ICP-MS analysis. Of the volunteers, 153 of them, 81 from Butte and 72 from Bozeman, also submitted sufficient volume of blood for ICP-MS analysis.

To determine potential environmental routes of metal exposure, soil samples were collected from 32 residences from Butte volunteers. Residential soil results were compared to MT-DEQ published

Table 5
Average, median and concentration range was determined for 35 elements found in Butte soil. Eleven of these elements were compared to available MT-DEQ background concentrations from 2 locations in both Silver Bow (SB1 and SB2) and Gallatin counties (G1 and G2) (Montana DEQ, 2013).

Soil Location		Fine soil fraction (< 250 μm) Concentrations (mg/kg)										
		Al	As	Cd	Co	Cr	Cu	Mn	Pb	Sb	Se	Zn
Butte (n = 32)	Avg.	4476	32.6	1.3	6.4	32	232	751	122	2.3	nd	388
	Median	4177	24.1	0.9	6.4	27	138	585	69	1.6	nd	243
	Range	2391–4197	22–74	0.7–3	5.4–15	15–71	90–811	454–2134	26–408	0.8–6.6	nd	95–3718
Silver Bow County	SB1	15,600	19.7	0.4	3.0	8.5	50.3	1560	24	0.2	0.2	89
	SB2	21,500	40.5	1.6	7.5	36.0	103.0	387	36.5	0.6	0.2	121
Gallatin County	G1	9920	6.5	0.4	4.1	21.0	50.4	739	8.6	nd	0.3	64
	G2	17,600	6.5	0.3	5.0	23.3	32.1	615	23	0.3	0.2	59

background concentrations (MTDEQ, 2013), and Cu, Pb, and Zn were found to be consistently higher than background. Some samples had higher than allowable EPA limits for As (40 ppm). Four months of air monitoring determined that particulate contained As and Mn levels above published limits (ATSDR, 2007; Chi-Chen and Lippmann, 2009; ATSDR, 2012) during the majority of weeks sampled. Based upon this environmental data, soil and/or air could be a plausible metal exposure route for individuals living within Butte city limits.

Arsenic is the most abundant element in the environment due to natural or human activities, including volcanic activity, contamination from mining and smelting, and its use in pesticides and medicines used to treat animals and sometimes humans (Lazo et al., 2003; Murphy and Aucott, 1998; Smedley and Kinniburgh, 2002). Arsenic is a metalloid and is usually found in different forms (organic and inorganic) and in various oxidation sates, with the inorganic forms (arsenite, arsenate) of arsenic considered to be more hazardous (Khan et al., 1997; Jomova et al., 2011). According to the International Agency for Research on Cancer (IARC, 1980) inorganic arsenic is classified as a human carcinogen, causing skin, lung and bladder cancer. Arsenic is also associated with many non-cancerous outcomes like cardiovascular dysfunction (Chen et al., 2011; Medrano et al., 2010; Sohel et al., 2009), adverse pregnancy outcomes (Ahmed et al., 2011), cognitive deficits (Wasserman et al., 2007), and type-2 diabetes (Navas-Acien et al., 2008). A limitation to the findings in this study is the lack of speciation of arsenic found at elevated levels in the Butte population. In order to more accurately assess the risk to the human population due to arsenic exposure, additional sampling should take place and speciation studies should be completed. In addition, future arsenic samples should be monitored by measurement of urinary arsenic levels as well as hair analysis. Urinary arsenic levels are generally accepted as the most reliable indicator of recent arsenic exposure (ATSDR, 2007).

Manganese is an essential trace micro-nutrient that plays an essential role in various physiological processes (Chen et al., 2015). There are well documented toxic effects from excess Mn exposure, which was first described in 1897 by James Couper and described as a neurological disease ("manganism") (Lucchini et al., 2009). Inhalation exposure to Mn-containing dusts and fumes may overload the natural homeostatic regulation of systemic Mn which has been shown in welders, an

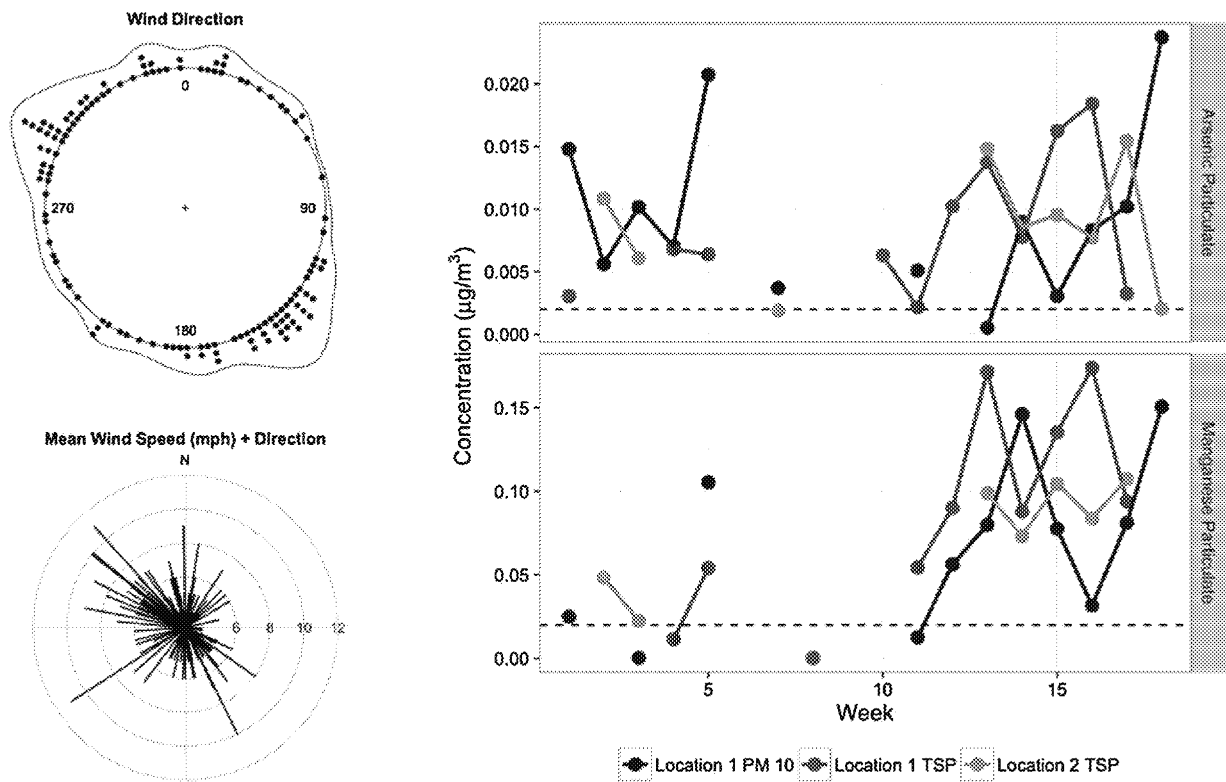

Fig. 4. Air particulate data over an 18 week period. Three air monitors, two monitoring for total suspended particulate and one PM 10 μm, were placed in two locations in Butte. Air filters were changed weekly and analyzed by ICP-MS for 11 elements. Arsenic and manganese concentrations are shown in comparison to typical national average (dashed line) (ATSDR, 2007; Chi-Chen and Lippmann, 2009; ATSDR, 2012).

occupationally exposed population (Pesch et al., 2012; van Thriel et al., 2017). The neurotoxicity of low-level exposure to Mn has been investigated mainly in small cross-sectional studies by testing cognitive and motor functions (Greiffenstein and Lees-Haley, 2007; Meyer-Baron et al., 2013). Studies of environmentally exposed adults reported attention impairments, poorer postural stability, and subclinical motor impairments at environmental air exposures > 0.1 μg Mn/m^3 (ATSDR, 2012). Notably, the air data collected for four months in Butte contained Mn particulate at or above the 0.1 μg Mn/m^3 level for several of the weeks sampled.

5. Conclusions

With over 100 years of mining and smelting activity and on-going mining activity, this study illustrates the need for continued testing to fully understand the potential health risks to individuals living in this area. In order to more fully understand the dynamics between historic mining, current mining, and natural surface geology and how these factors might be impacting human health, additional data from volunteers should be collected. Bioavailability studies, including metal speciation studies, would need to be undertaken to fully assess human exposure routes. Air monitoring for larger particulate matter and identification of the metals contained in the particulate, should also be a focus of future studies.

Conflict of interest

None.

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